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16. ABSTRACT

Measurements of 0600 to 0900 AM speciated NMOC compounds obtained from 19 urban areas located throughout the United States during a 1985 sampling program are presented. The cities sampled all experienced ozone levels above the National Ambient Air Quality Standard (NAAQS) of 0.12 ppm. Speciated NMOC information is useful for both the development of photochemical ozone models and the evaluation of the sources contributing to ambient air concentration levels. Using a simple box model it appears that NMOC composition has the greatest impact on ozone formation at the lower NMOC to NO_x ratios.

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The Measurement of Oxidant Precursors and Their Relationship to Ozone Formation

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Abstact

During the summer periods of 1984 through 1986 measurement of 0600 to 0900 AM nonmethane organic carbon (NMOC) and nitrogen oxides (NO_x) were made at various cities throughout the United States. The cities sampled all experience ozone levels above the U.S. National Ambient Air Quality Standard (NAAQS) of 0.12 ppm. Detailed NMOC measurements were performed on approximately 10 to 20% of the samples collected. This paper presents speciated NMOC information for the 19 sites sampled during the 1985 study. Speciated NMOC information is useful for both the development of photochemical ozone models and the evaluation of sources contributing to the ambient air concentration. It appears that NMOC composition has the greatest impact on ozone formation at the lower NMOC to NO_x ratios.

INTRODUCTION

Measurement of nonmethane organic carbon (NMOC) compounds and nitrogen oxides (NO_x) during the 0600 to 0900 AM period was conducted at several urban areas throughout the United States from 1984 through 1986. The urban areas studied all have been identified as non-attainment areas of the United States National Ambient Air Quality Standard (NAAQS) for ozone (Federal Register, 1983). By law the States in which these cities are located are required to provide precursor control strategy to bring these areas into ozone attainment. These control plans are referred to as State Implementation Plans (SIP). Current control strategy guidance relate afternoon ozone concentrations to 0600 to 0900 AM precursor levels (EPA, 1981). Previously states used continuous total hydrocarbon analyzers to measure ambient air NMOC concentrations. These analyzers, however, have been shown to be inaccurate and unreliable for NMOC measurements at ambient air concentrations (McElroy 1975, Harrison 1977, and Richter 1983). A new approach was offered to the states to measure NMOC accurately at concentrations below 100 ppbC. This approach involved the cryogenic preconcentration of ambient air prior to injection into a flame ionization detector (FID) and is referred to as a preconcentration direct flame ionization detector (PDFID) (McElroy 1986). The measurement approach removes air and methane from the air sample permitting direct determination of NMOC.

In the cities studied samples were collected in stainless steel containers and shipped to a central laboratory located at the Research Triangle Park, North Carolina for analysis (McElroy 1985). Approximately 10 to 20% of the air samples were selected for detailed gas chromatographic analysis. The GC analyses were used for both quality assurance (QA) of the PDFID procedure and to determine NMOC composition in the urban area studied. A diversity of cities were

studied that included those dominated by vehicular traffic while other areas contained major petrochemical sources. The NMOC compositional measurements determined in these studies will be useful in the development of the chemical mechanisms used in ozone photooxidation models and to perform sensitivity tests to determine models accuracy for ozone predictions.

To date 36 cities have been sampled during the 3-year period from 1984 to 1986. The purpose of this paper is to present and compare the NMOC results obtained in some of the cities studied. The NMOC results from the 1985 Nineteen City Study were selected for presentation in this report.

EXPERIMENTAL

The sample collection device and the PDFID system used for these studies have been published elsewhere (McElroy 1985). The publication contains detailed information concerning the sample canisters, the sample collection device, and the PDFID analysis system.

Details of the GC system and the preconcentration procedure have been published elsewhere (Seila 1986). The column used was a 60m x 0.32 mm i.d. DB-1 fused silica column (J&W Scientific, Cordova, CA). The helium carrier gas flowrate was maintained at 2 to 3 cm^3 min^{-1}. The column temperature conditions consisted of an initial 1 min hold at -50°C followed by temperature programming at 8°C/min to a final temperature of 200°C with a final hold time of 5 min. Calibration of the individual compound peaks was performed with a National Bureau of Standards (NBS) 2.84 ppm propane in air Standards Reference Material (SRM) No. 1665b cylinder. A single response factor was used to determine all GC peak concentrations. This approach has been determined to be valid for most hydrocarbon compounds (Deitz 1967). Canister samples were generally analyzed on the GC system within 2 to 4 days after collection.

At least one sample from each city studied was re-analyzed with chemical stripper columns (Klosterman 1967, Lonneman 1983). A 10 cm X 1.25 cm stainless steel column packed with mercuric sulfate-sulfuric acid mixture coated on 40-60 mesh Chromasorb P was used to remove olefinic hydrocarbon peaks from the air sample. A similar 10 cm X 1.25 cm stainless steel column packed with silver sulfate-sulfuric acid mixtrue on 40-60 mesh Chromasorb P was used to remove all aromatic peaks except benzene which is approximately 60% removed.

RESULTS AND DISCUSSION

The urban sites included in the 1985 Nineteen City Study are listed in Table I. Actually only 18 cities were studied since 2 sites were located in Philadelphia. Eight of the cities studied were located in the state of Texas with 5 of these cities situated on the industrialized southeast coast of the state. Two criteria were used in the selection of samples for GC speciation analysis. First, the selected samples for all sites were equally distributed over the entire sampling period. An attempt was made to select an equivalent number of Monday, Tuesday, Wednesday, Thursday, and Friday samples to avoid possible day-of-week bias. Second, samples collected at sites that experienced afternoon ozone which exceeded 0.12 ppm were selected. It was anticipated that the GC analyses for high ozone days would be particularly useful to the states for their modeling studies. The latter criteria may have resulted in a biased high average NMOC concentration for the GC samples at these sites since usually high precursor concentration are observed on days of high afternoon photochemical ozone levels. However, NMOC emission patterns are expected to be somewhat consistent on a day to day basis. Consequently NMOC composition is not expected to be significantly different on these high ozone days.

Figure 1 shows a comparison of mean NMOC concentration by site for all samples analyzed with the PDFID procedure with those selected for detailed GC analysis. The general comparability between the two measurement procedures is quite reasonable. The two sites that show significant disagreements are the Philadelphia sites 13 and 14. The GC means are approximately 25% higher than the PDFID means. For these two sites during the 1985 study pre-selection sample bias may be a legitimate explanation. Several samples were analyzed as the result of high afternoon ozone levels observed in the Philadelphia area. The mean NMOC levels observed at these sites range from approximately 0.40 ppmC at Boston, MA to about 1.8 ppmC at Beaumont, Texas.

The number of GC peaks observed at the sites ranged from about 100 on low NMOC concentration days to more than 240 peaks on the higher NMOC concentration days. Currently 65 of the GC peaks have been identified and verified by retention time location using pure hydrocarbon compounds. Consequently for high NMOC samples more than 175 GC peaks remain unidentified. In an effort to determine some information of these peaks, selected samples were re-analyzed using stripper columns selective for the removal of olefinic and aromatic compounds (Klosterman 1967, Lonneman 1983). Using this approach on assignment of the unidentified peaks as paraffinic, olefinic and aromatic could be made. At least one pair of stripper column analyses were performed for each urban site sampled in 1985. No surprises were experienced by comparison of stripper column results from site to site. The same paraffin, olefin, or aromatic identifications were assigned to the similar retention time unknown peaks observed in the different cities. Using the hydrocarbon classification assignments determined from the stripper column analyses, bar charts of known and unknown paraffins, olefins, and aromatics are presented respectively for each site in Figures 2, 3,

and 4. As can be observed from the figures, the majority of the hydrocarbon mass for each hydrocarbon classification group is accounted for as known hydrocarbon compound. This demonstrates that the unknown peaks, even though more abundant than known peaks, have quite low ambient air concentrations. Reviewing the results in Figures 2, 3, and 4 indicates that a larger percentage of the aromatic comppound mass is unknown compared to the paraffinic and olefinic compounds. The reason for this is that the largest unknown peaks have been tentatively identified as aromatic compounds. From Figures 2, 3, and 4, it appears that the Beaumont, Texas site has the highest average percentage of unknown compound mass of any of the 19 sites sampled in 1985.

Determination of the sources contributing to the NMOC levels observed in the cities studied is quite a difficult task since similar hydrocarbon compounds are released by vehicular and industrial sources. Source hydrocarbon compositions have been utilized in an effort to characterize NMOC composition in urban ambient air (Mayrsohn 1976, Scheff 1986). These procedures have been somewhat successful in the evaluation of source contribution, however, many more source compositional measurements are required to further develop these techniques. An approach to characterize NMOC source contribution is the use of acetylene as a tracer of vehicular tailpipe emissions. Acetylene is nearly unique to the vehicular combustion process except in those urban areas where it is manufactured or is used in industrial processes. Also acetylene possesses a long atmospheric lifetime of approximately 150 days which is important for its use as a vehicular tracer. To utilize acetylene as a tracer, a source area dominated by vehicular traffic is required. A tunnel was selected as the sampling location since it is dominated by vehicular tailpipe emissions. It is also thought

that the tunnel atmosphere is representative of a large number of vehicles and fuel types used in typical urban areas. Ratios of NMOC compounds and sum of NMOC compounds to acetylene were determine in the Lincoln Tunnel (Lonneman 1986). Some of the ratios determined are shown in Table II. To calculate estimated vehicular concentrations the average acetylene concentration observed at a site is multiplied by the ratios given in Table II. These calculations were performed for the sum of paraffins, olefins, and aromatics at the cities studied in 1985 and are given in Figures 5, 6, and 7. Significant non-vehicular paraffin sources are observd in all cities as shown in Figure 5. Typically the vehicular paraffin estimate at most sites is 50% or less of the total paraffins. This relatively low vehicular contribution of the paraffins is not surprising since significant concentrations of ethane and propane from natural gas and n-butane and isopentane from gasoline evaporative sources are generally observed in most urban areas studied. More than 90% of the paraffins measured at Beaumont, TX are from non-vehicular sources. Review of Figure 6 suggests that 90% or greater of the total olefins at most sites can be accounted for from vehicular sources. Non-vehicular olefins sources are however observed at the Beaumont, Clute, Houston, Orange, and Texas City, TX sites. Beaumont, TX again shown the most abundant non-vehicular olefin sources. In Figure 7 it appears that significant non-vehicular aromatics are suggested for many of the cities. However at 5 of the 19 sites vehicular contribution exceeds 80%.

Comparison of paraffin, olefin, and aromatic compositions at the 19 sites are shown in Figure 8. Typically the paraffins are the most abundant species of hydrocarbon at all sites ranging from 45 to 60% of the total NMOC. Aromatic hydrocarbons are generally

the next most abundant hydrocarbon type ranging from 20 to 30% of total NMOC. Olefins are the least abundant class of hydrocarbon ranging from 15 to 20% of total NMOC. This general compositional breakdown, however, is not observed at the industrial-urban sites on the southeast coast of Texas. At Beaumont, TX (Site 1) and Clute, TX (Site 5) the olefin content is significantly greater than the aromatic fraction. Ozone formation from such a diversity of NMOC composition are expected to be quite different. To test this hypothesis, 12 hour photochemical ozone model simulations were performed using the carbon bond (CB) IV chemical mechanism for three urban areas with drastically different NMOC compositions. Table III contains the compositional breakdown of Beaumont, TX, Washington, DC, and Lake Charles, LA in CB (IV) notations. Beaumont, TX was selected because of its high paraffinic content which resulted in the largest PAR fraction observed among the 19 sites studied in 1985. High olefinic content of the NMOC measured at Beaumont also resulted in an OLE fraction that too was larger than any of the other 18 sites. Highest aromatic content was observed at Washington, DC and resulted in the highest TOL and XYL fraction observed at the 19 sites. The NMOC composition at Lake Charles, LA contained the largest contribution of nonreactive compounds observed at the 19 sites and consequently the largest NR fraction. Simulations at NMOC to NO_x ratios of 6, 12, and 24 to 1 were performed. Initial conditions and other input parameters used for these simulations are given in Table III.

Ozone profiles of the 12 simulation results are given in Figures 9, 10, and 11. At the lowest NMOC to NO_x ratio (Figure 9), a significant difference is observed between Lake Charles ozone profile and the profiles determined at the other two sites. The large NR fraction at Lake Charles has significantly reduced ozone

maximum and increased the time when ozone maximum is observed. Some small differences are observed between the Beaumont, TX and Washington, DC profiles, however, the overall reactivity of the two NMOC compositions appear to be comparable. As the NMOC to NO_x ratios are increased (Figures 10 and 11), differences in the ozone profiles seem to disappear. This is particularly true in the case at the 24 to 1 ratio (Figure 11) where the ozone profiles at all three sites appear to intertwine. Applying these results to the ambient air suggest that NMOC reactivity is more important at lower NMOC to NO_x ratios.

CONCLUSIONS

Conclusions of the NMOC results measured in the 1985 Nineteen Cities Study are three-fold. First, the largest GC peaks observed in these cities have been identified consequently the largest fraction of NMOC mass is known. Secondly, hydrocarbon compositional information is quite useful for the evaluation of source contribution and ultimately to the control of hydrocarbon precursors. Lastly, hydrocarbon compostion appears to have a greater effect on ozone formation at lower NMOC to NO_x ratios.

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TABLE I

Site Identifications For The 1985 Nineteen City Study

Site ID	Site Abbreviation	Site Number
Beaumont, TX	BMTX	1
Boston, MA	BOMA	2
Baton Rouge, LA	BRLA	3
Cleveland, OH	CLOH	4
Clute, TX	CLTX	5
Dallas, TX	DLTX	6
El Paso, TX	ELTX	7
Fort Worth, TX	FWTX	8
Houston, TX	HSTX	9
Kansas City, MO	KCMO	10
Lake Charles, LA	LCLA	11
Orange, TX	ORTX	12
Philadelphia, PA (1)	A1PA	13
Philadelphia, PA (2)	P2PA	14
Portland, ME	PTME	15
Richmond, VA	RVA	16
St. Louis, MO	SLMO	17
Texas City, TX	TCTX	18
Washington, DC	WDC	19

TABLE II

Selected NMOC Compound and Sum of NMOC Compounds to
Acetylene Ratios Determined from the 1982 Lincoln Tunnel Study

Component	Ratio
n-Butane	1.21 ± 0.19
Toluene	1.89 ± 0.13
Propene	0.78 ± 0.08
Sum of Paraffins	10.53 ± 1.30
Sum of Olefins	6.03 ± 0.63
Sum of Aromatics	9.58 ± 0.73
Sum of NMOC	26.0 ± 2.10

TABLE III

Carbon Bond IV Fractions for Three 1985 Cities and Other
Model Input Conditions for 12 Hour Photooxidation Simulations

CB IV Fraction	Beaumont, TX	Washington, DC	Lake Charles, LA
OLE	0.076	0.031	0.017
PAR	0.656	0.523	0.589
TOL	0.067	0.132	0.070
XYL	0.057	0.132	0.073
HCHO	0.021	0.022	0.021
ALD2	0.034	0.055	0.048
ETH	0.023	0.039	0.018
NR	0.068	0.070	0.172

Model Input Conditions

Mixing Height Rise from 250 to 1235 meters
Los Angeles Summer Solstice
Ozone Aloft was 0.05 ppm
Temperature was 303°A
H_2O was 25,000 ppm (50% RH)
Initial NO_x Composition was 75% NO and 25% NO_2
Simulation Time Period 8 AM to 8 PM

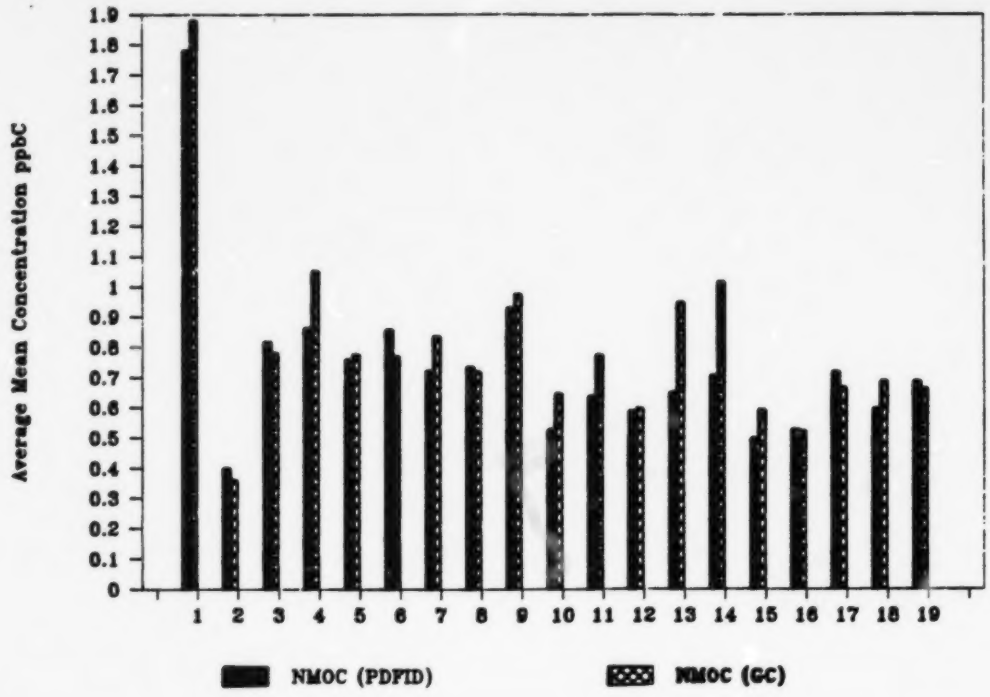

Figure 1. Comparison of average mean concentration obtained with the PDFID and GC procedures for cities sampled in the 1985 Nineteen Cities Study

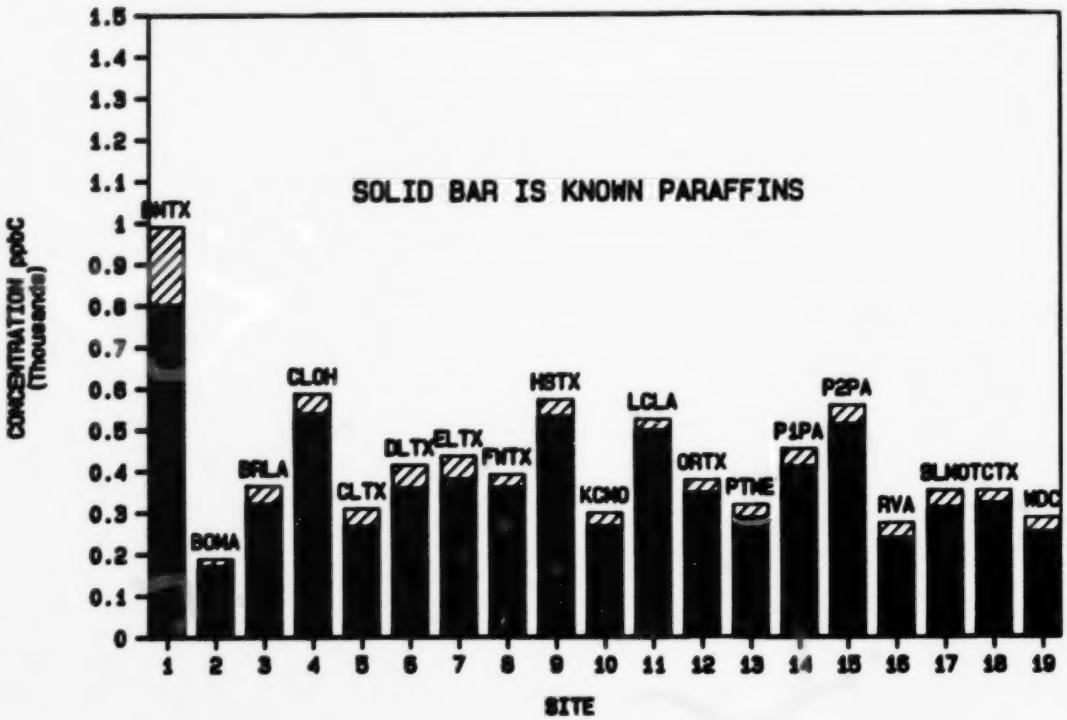

Figure 2. Sum of known and unknown mean paraffin concentrations obtained at the 19 sites in the 1985 study

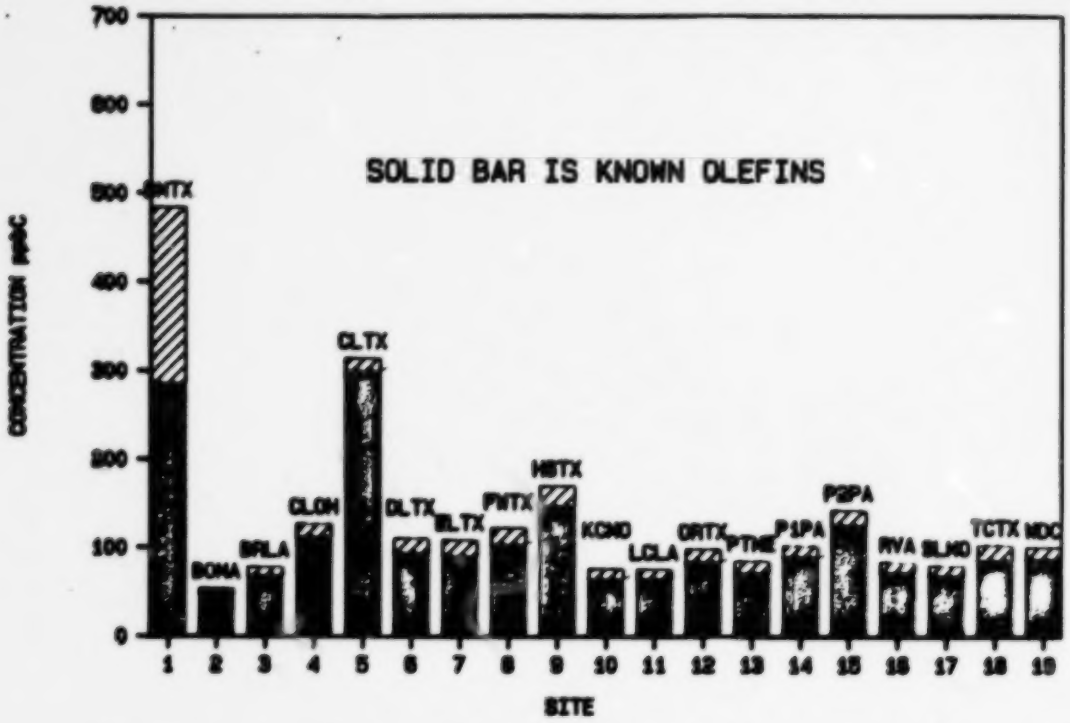

Figure 3. Sum of known and unknown mean olefin concentrations obtained at the 19 sites in the 1985 study

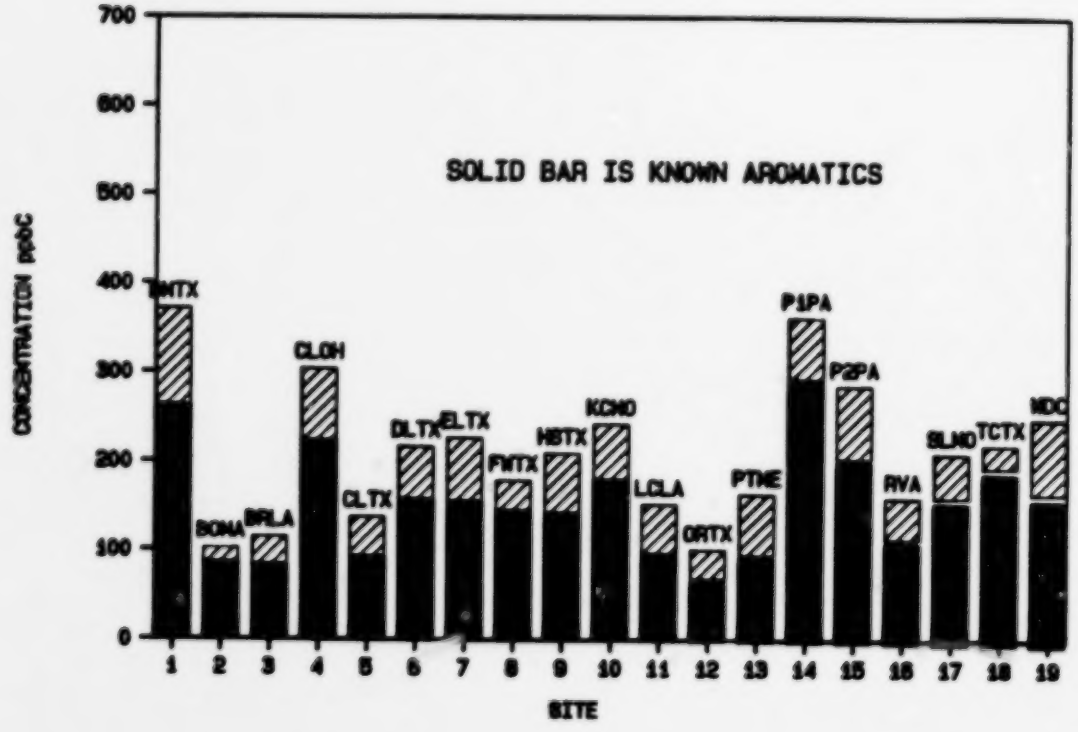

Figure 4. Sum of known and unknown mean aromatic concentrations obtained at the 19 sites in the 1985 study

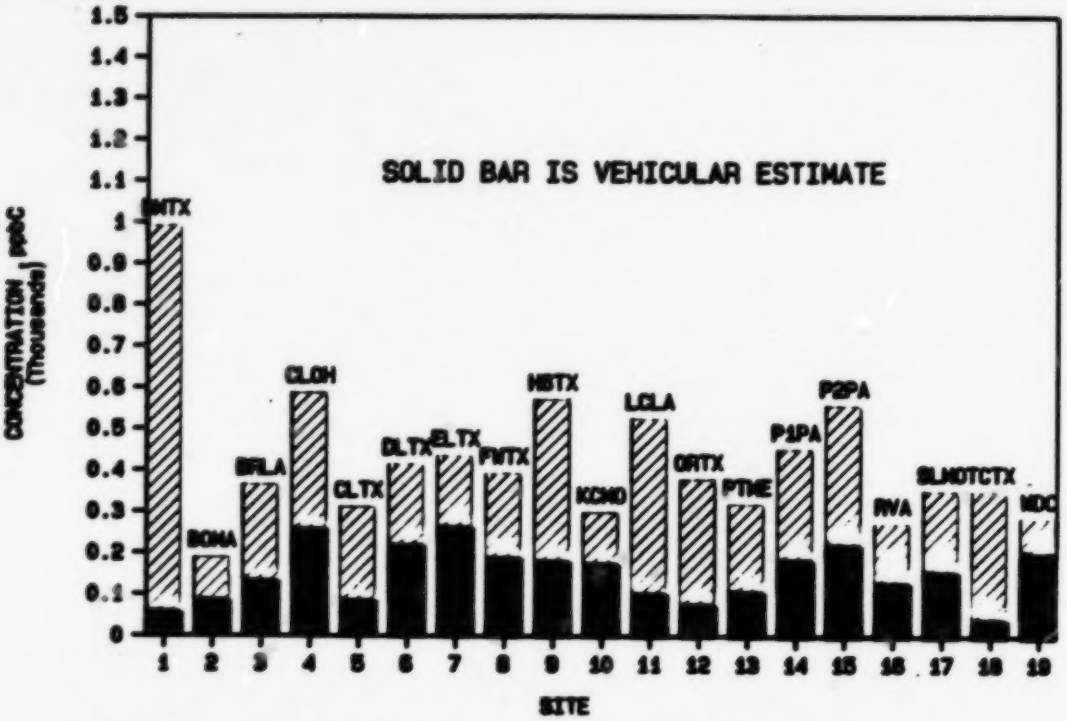

Figure 5. Vehicular and non-vehicular paraffin estimates calculated for the 19 sites in the 1985 study

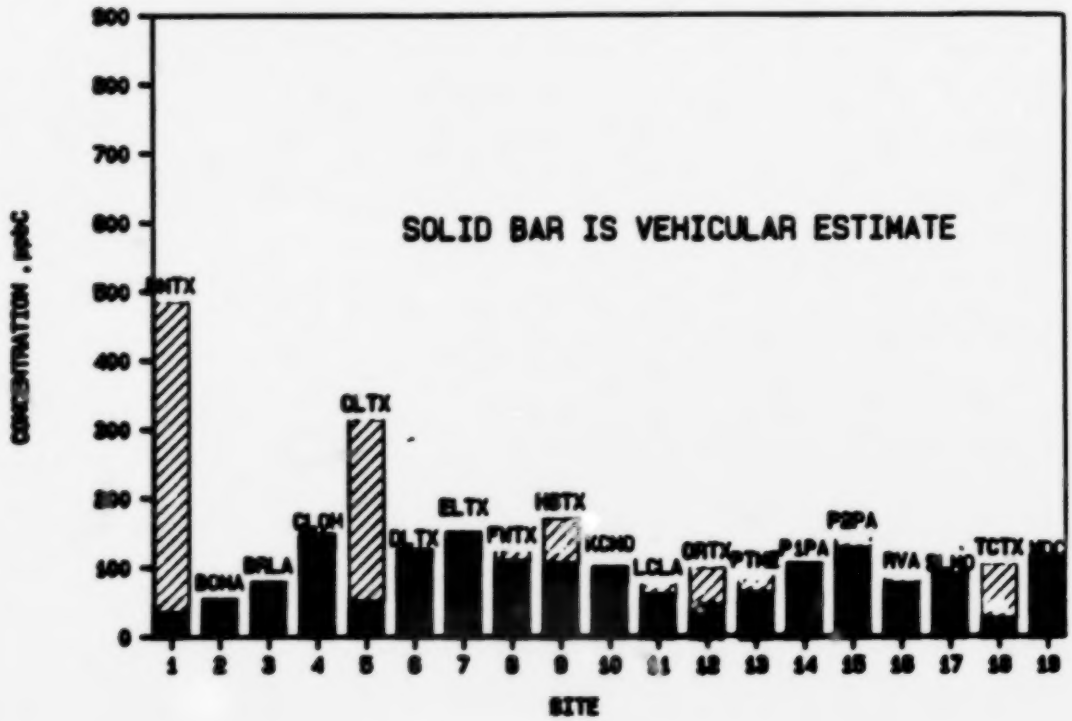

Figure 6. Vehicular and non-vehicular olefin estimates calculated for the 19 sites in the 1985 study

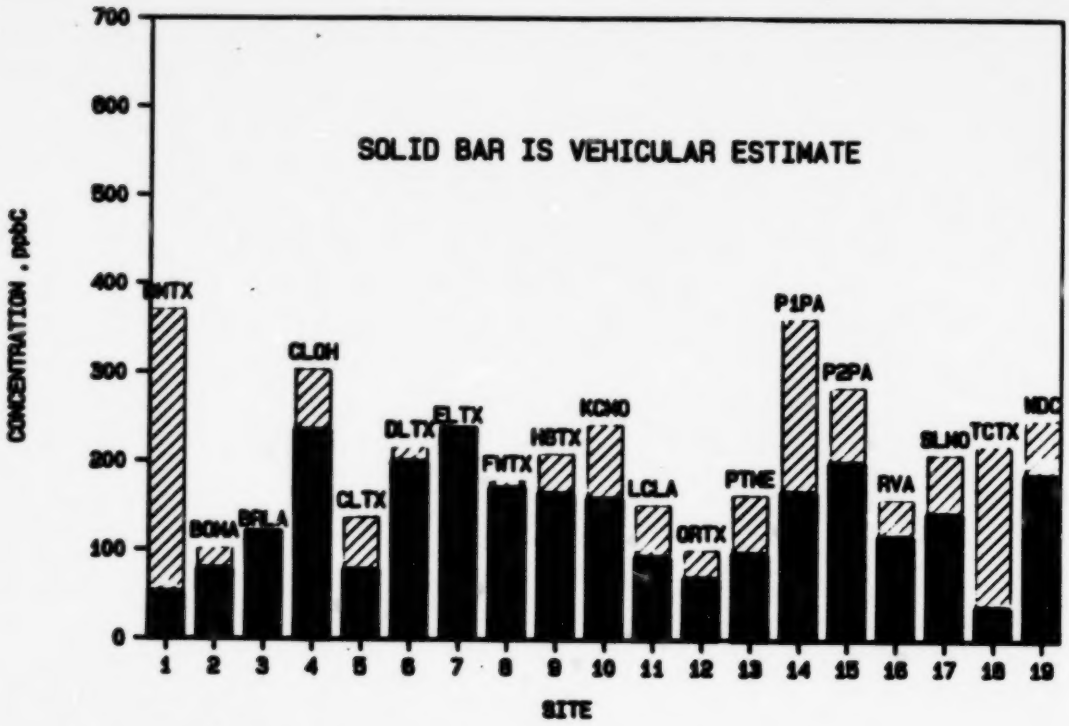

Figure 7. Vehicular and non-vehicular aromatic estimates calculated for the 19 sites in the 1985 study

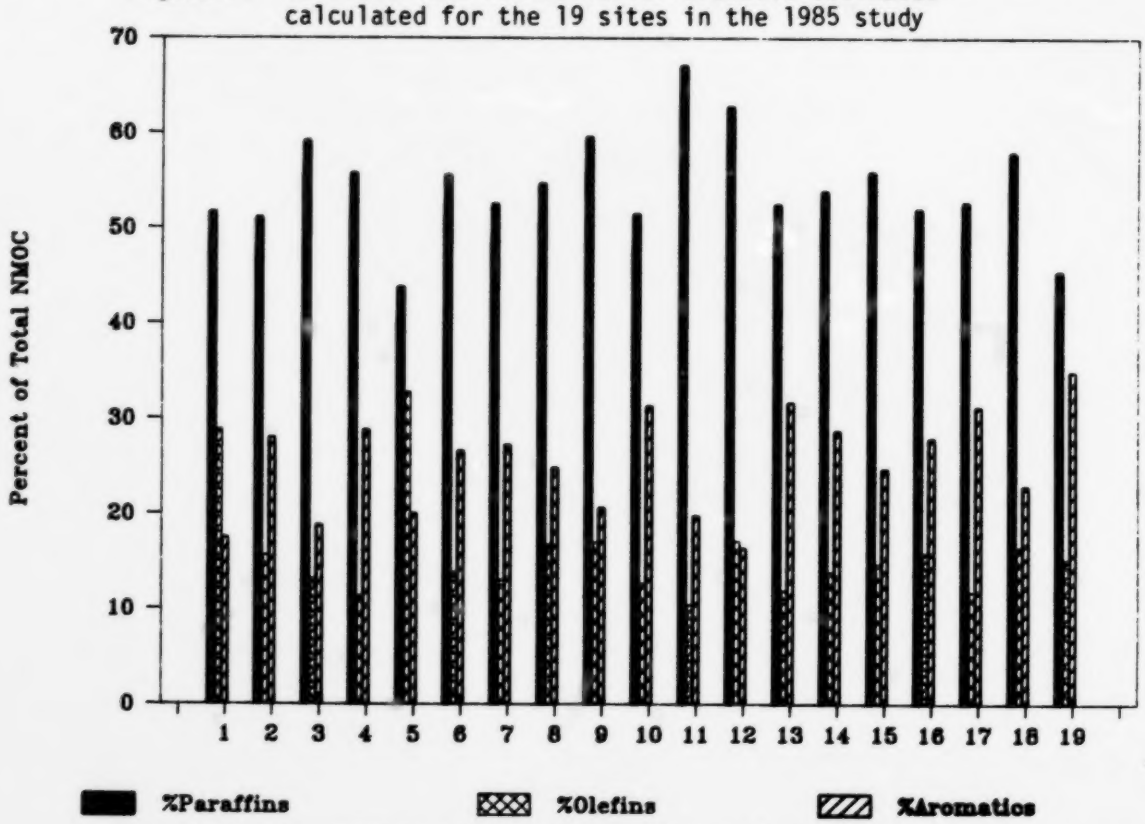

Figure 8. Percentage paraffins, olefins, and aromatics composition for the 19 sites participating in the 1985 study

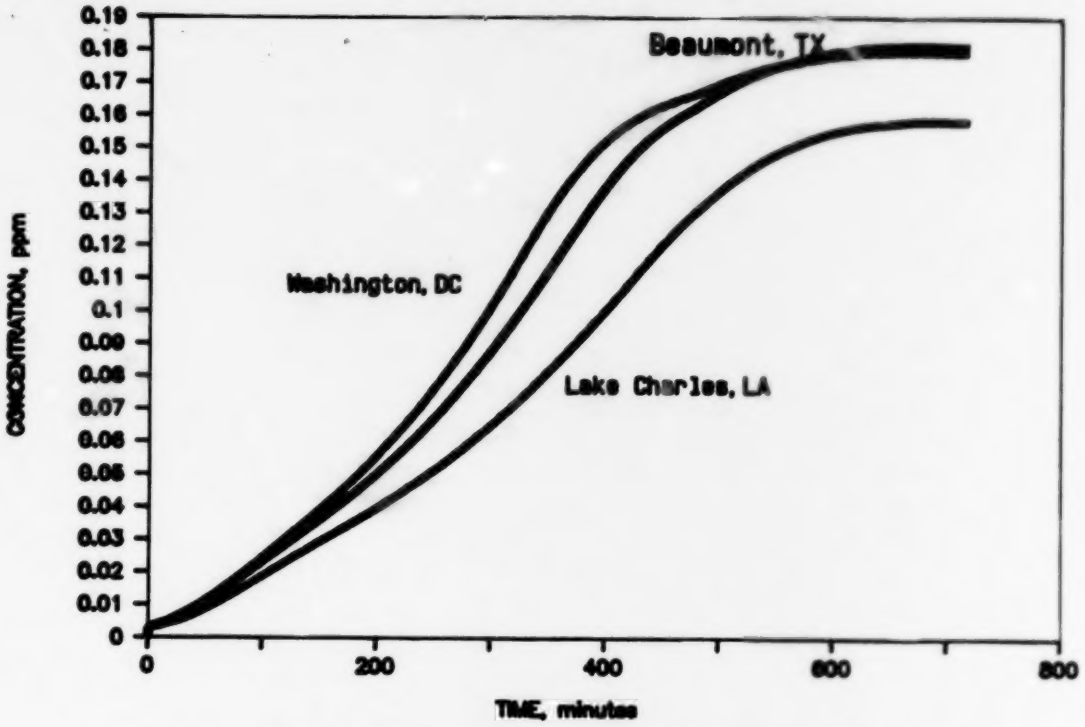

Figure 9. Ozone profiles for 12 hour simulations performed for Beaumont, TX, Washington, DC, and Lake Charles, LA using an NMOC to NO_x ratio of 6

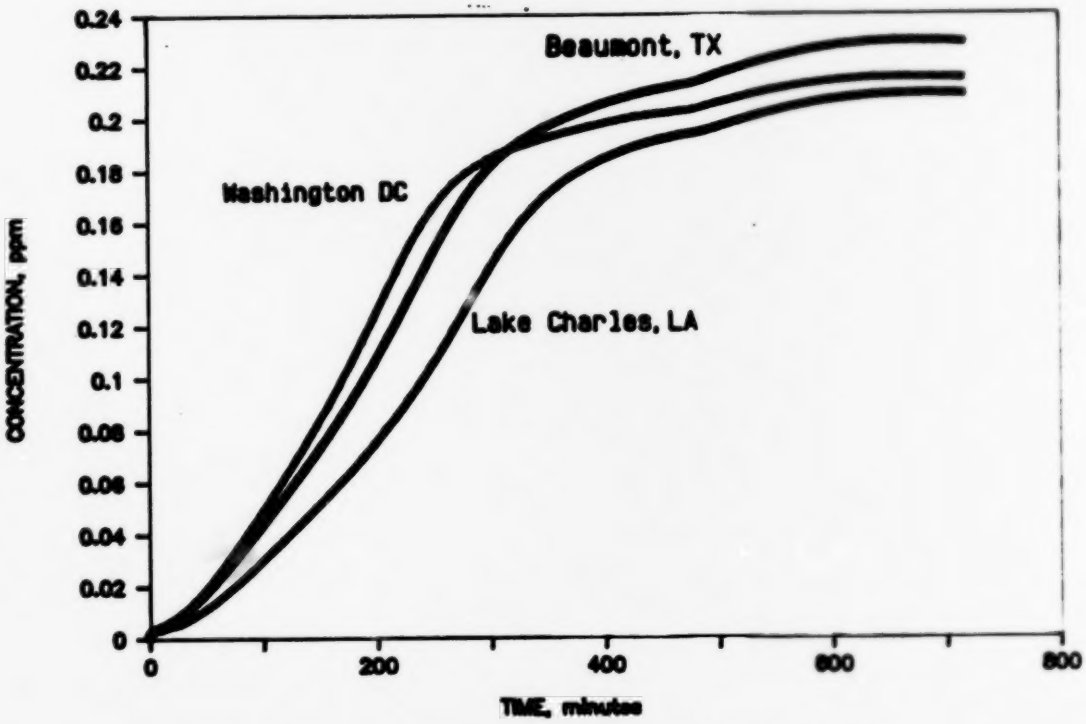

Figure 10. Ozone profiles for 12 hour simulation performed for Beaumont, TX, Washington, DC, and Lake Charles, LA using an NMOC to NO_x ratio of 12

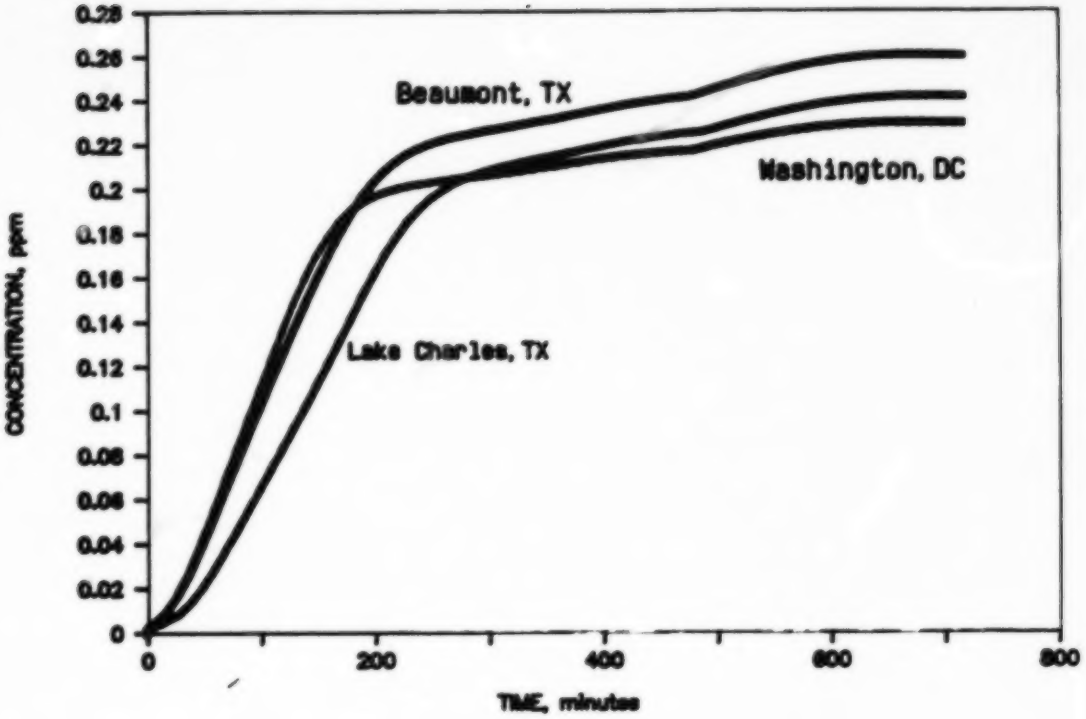

Figure 11. Ozone profile for 12 hour simulations performed for Beaumont, TX, Washington, DC, and Lake Charles, LA using an NMOC to NO_x ratio of 24